

REMARKS

The final office action of July 22, 2003 has been reviewed and the Examiner's comments carefully considered. Claims 15-28 have been cancelled as these claims are directed to a non-elected invention. Applicants expressly reserve the right to file a divisional application directed to the subject matter of claims 15-28.

Applicants acknowledge withdrawal of the rejection of claims 1-14 over Soltwedel under 35 U. S. C §103(a).

Claims 1-10, 13 and 14 have been rejected under 35 U. S. C §103(a) as being unpatentable over Berger et al. and Young et al. in view of Japanese Patent No. 7-331164. Note that Applicants have submitted herewith a translated copy of the entire Japanese patent. The Examiner asserts that Berger et al. discloses a weldable coating composition comprising an epoxy-containing material in combination with aminoplasts or isocyanates as curing agents and electroconductive pigments. The Examiner also asserts that Young et al. likewise discloses weldable coating compositions comprising an epoxy-containing material, an aminoplast curing agent, and electroconductive pigments. The Examiner relies on Young et al. for a teaching of the use of the epoxy-containing material at 60-90 percent by weight.

The Examiner concedes that neither Berger et al. nor Young et al. recites the claimed reaction product of the epoxy resin with a phosphorus acid groups-containing compound. The Examiner relies on the Japanese reference for the teaching of the use of such a reaction product in a coating composition. The Examiner suggests that the motivation to combine the teachings of the references lies in a statement from the Japanese reference indicating that the compositions described therein demonstrate "good storage stability and coatability, and forms coatings with good adhesion, water resistance, and fabrication properties."

Applicants respectfully disagree with the Examiner's rejection of the claims. Neither Berger et al. nor Young et al. teach or suggest the claimed reaction product of the epoxy resin with a phosphorus acid groups-containing compound. Further, while Young et al. teaches the use of an epoxy resin at 60-90 percent by weight, it does not teach the use of a reaction product of the epoxy resin with a phosphorus acid groups-containing compound at such levels. The Japanese reference does nothing to overcome the deficiencies of the two primary references in teaching or suggesting the claimed composition. In paragraph [0011] of the Japanese reference, it is noted that the use of excess phosphoric acid in the preparation of modified epoxy resins may cause "a significant problem of reduced adhesive properties".

Since the compositions of the primary references already demonstrate excellent adhesion (see Young et al., Field of the Invention), one skilled in the art would not be led to modify the compositions of the primary references by using a phosphorus acid-modified epoxy resin as taught by the Japanese reference, lest it cause reduced adhesion. Moreover, even if one skilled in the art were to use the phosphorus acid-modified epoxy resin as taught by the Japanese reference, the amount would be in the range of only 0.1 to 20 percent by weight. As stated in the reference at paragraph [0015], from the standpoint of adhesive properties and moisture resistance, the content of the modified epoxy is preferably 0.1 to 20 percent by weight. One skilled in the art would not be led to use the phosphorus acid-modified epoxy resin at higher levels because of the risk of reduced adhesive properties and moisture resistance indicated by the Japanese reference.

In conclusion, because of the individual teachings of each reference, none of the references, taken alone or in any combination, teach or suggest the claimed composition; i. e., a curable coating composition comprising

- a. a resinous binder comprising:
 - i. a reaction product of an epoxy-containing polymer with a compound containing phosphorus acid groups, the reaction product being present in the composition in amounts of 50 to 90 percent by weight of the resinous binder and having reactive functional groups, and
 - ii. a curing agent having functional groups reactive with the functional groups of (i), the curing agent being present in the composition in amounts of 10 to 50 percent by weight of the resinous binder; and
- b. an electroconductive pigment dispersed in (a) such that the weight ratio of b to (i) plus (ii) is within the range of 0.5 to 9.0:1,

the curable coating composition being characterized such that when it is deposited and cured on a metal substrate, the cured coating is weldable. Reconsideration and withdrawal of the rejection is respectfully requested.

Claims 1-10, 13 and 14 remain in the application. It is respectfully submitted that the application is in condition for allowance. A favorable action is respectfully requested for the reasons discussed above.

Respectfully submitted,

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August 28, 2003

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SEP 04 2003
TC 1700

(19) Japan Patent Office (JP)
(12) KOKAI TOKKYO KOHO (A)
(1) Laid-open Application Number: 7-331164
(4) Publication Date: December 19, 1995

(51) Int. Cl. ⁶	Id. No.	Office Reg. No.	F1	Techn. Ind. Field.
C 09 D 163/00	PJM			
	PKG			
C 09 D 161/20	PHK			
C 09 D 175/004	PHP			

Examination Request: None

No. of Claims: 8 OL (total pages 6)

(21) Application No. 6-131806
(22) Application Filed: June 14, 1994

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(54) [Title of the Invention] RESIN COMPOSITION FOR COATING AND COATED STEEL SHEET

(57) [Abstract]

[Structure] A composition prepared by blending a reaction product of an epoxy resin of bisphenol A type with phosphoric acid, a polyester resin containing hydroxyl groups, and a methylated melamine resin is used as an undercoat for a precoated metal.

[Effect] Excellent adhesive properties, water resistance, and processability.

[Patent Claims]

[Claim 1] A thermosetting resin composition for coating comprising a modified epoxy resin(A) having a structure obtained by reacting phosphoric acid with epoxy groups of epoxy resin, a polyester resin (B) containing hydroxyl groups, a curing agent (C) as the necessary components.

[Claim 2] The composition as described in claim 1, wherein the modified epoxy resin (A) has a structure obtained by reacting phosphoric acid with an epoxy resin with an epoxy equivalent of 150-5,000.

[Claim 3] The composition as described in Claim 1 or Claim 2, wherein the modified epoxy resin (A) is obtained by conducting a reaction of hydroxyl groups bonded to phosphorus atoms in phosphoric acid with epoxy groups in the epoxy resin at a ratio of the former to the latter of 0.05-0.95 in equivalent ratio.

[Claim 4] The composition as described in Claim 1, Claim 2, or Claim 3, wherein the polyester resin (B) containing hydroxyl groups has a number-average molecular weight of 5,000-30,000.

[Claim 5] The composition of any one of claims 1 through 4, wherein the curing agent (C) is an aminoplast resin or a blocked isocyanate resin.

[Claim 6] The composition of any one of claims 1 through 5, wherein the modified epoxy resin (A), polyester resin (B) containing hydroxyl groups, and curing agent (C) are compounded at the following ratios based on the total of (A)-(C): modified epoxy resin (A) 0.1-20 wt.%, polyester resin (B) containing hydroxyl groups 70-95 wt.%, and curing agent (C) 5-70 wt.%.

[Claim 7] The composition of claim 6 additionally containing a pigment.

[Claim 8] A coated steel sheet in which the composition described in claim 7 is coated on a steel sheet and then a thermosetting resin composition composed of a polyester resin (D) containing hydroxyl groups, an aminoplast resin (E), and a pigment (F) is coated as a top layer.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Utilization] The present invention relates to a thermosetting resin composition for coatings, more specifically to a resin composition for coatings that can form a coating film with excellent processability and moisture resistance and to a coated steel sheet.

[0002]

[Prior Art Technology] The so-called precoated metal obtained by coating a steel sheet with a thermosetting resin composition for coatings and then with a top layer has been widely used for walls, roofs, shutters, and lightweight electric apparatuses.

[0003] Compositions obtained by combining polyester resins, aminoplast resins, or block isocyanate resins have been widely used in recent years as undercoat coating materials because of their excellent processability.

[0004] Furthermore, for example, Japanese Patent Application Laid-open Heisei 2-212569 has suggested a coating composition for a single-coat finish, this composition containing a modified epoxy resin prepared by conducting a reaction of phosphoric acid and an alcohol with an epoxy resin, and also an acrylic resin or polyester resin, and an aminoplast resin as resin components.

[0005]

[Problems Addressed by the Invention] However, combinations of polyester resins and aminoplast resins have a sealing ability lower and the performance, such as moisture resistance, degraded by comparison with those obtained when epoxy resin is used and such combinations are unsatisfactory for precoated metals. Furthermore, even when the coating composition described in Japanese Patent Application Laid-open Heisei 2-212569 was applied to a precoated metal, not only the moisture resistance and corrosion resistance were poor, but also the coating stability was low.

[0006] Accordingly, it is an object of the present invention to provide a coated steel sheet excellent in adhesion of the coating to the steel sheet, stability of the coating material, and also water resistance and processability.

[0007]

[Means to Resolve the Problems] With the foregoing in view, the inventors have conducted an intensive study and have found that a coating material with excellent adhesive properties and stability and a coated steel sheet with excellent moisture resistance and processability can be obtained by using a coating material comprising an epoxy resin modified with phosphoric acid, a polyester resin containing hydroxyl groups, and a curing agent as the necessary components. This finding led to the creation of the present invention.

[0008] Thus, the present invention provides a thermosetting resin composition for coating, comprising a modified epoxy resin (A) obtained by reacting phosphoric acid with epoxy resin, a polyester resin (B) containing hydroxyl groups, and an aminoplast resin or blocked isocyanate resin as a curing agent (C).

[0009] the present invention also relates to a coated steel sheet obtained by coating the above-described composition blended with a pigment and the like as a primer coat and then top coating a thermosetting resin composition composed of a polyester resin (D) containing hydroxyl groups, an aminoplast resin (E), and a pigment (F).

[0010] No specific limitation is placed on the epoxy resin employed for the manufacture of the modified epoxy resin (A) in accordance with the present invention. For example, bisphenol A, bisphenol F, bisphenol S, phenol novolak, cresol novolak, bisphenol A novolak, and other glycidyl ether-type epoxy resins or β -methyl-glycidyl ether and other glycidyl ether type epoxy

resins can be used. The especially preferred among them are glycidyl ether type epoxy resins of bisphenol A type. No specific limitation is placed on the epoxy equivalent of those epoxy resins, but the preferred epoxy equivalent is within a range of 150~5,000 g/eq. Thus, if the epoxy equivalent is above 150 g/eq, the adhesive properties and moisture resistance are greatly improved. Furthermore, good mutual solubility with the polyester resin (D) containing hydroxyl groups and excellent stability of the coating material are obtained when the epoxy equivalent is no more than 5,000 g/eq. The especially preferred is the range of 500~4,000 g/eq because the above-mentioned effects are especially good within this range.

[0011] The modified epoxy resin (A) used in accordance with the present invention has a structure obtained by the reaction of the above-described epoxy resin with phosphoric acid. One of the methods for the manufacture of modified epoxy resins, for example, disclosed in Japanese Patent Application Laid open Heisei 2-212569, produces epoxy resins having a structure obtained by the reaction of an epoxy resin, phosphoric acid and then with a low-molecular alcohol. However, phosphoric acid usually has a reactivity with epoxy groups higher than that with low-molecular alcohols. Therefore, a large amount of phosphoric acid is required to obtain the above-mentioned openly disclosed structure. As a result, the low-molecular alcohol forms excess phosphoric acid compounds and phosphoric acid esters, causing a significant problem of reduced adhesive properties. Therefore such phosphoric acid esters are preferably not present in the composition. Accordingly, the reaction ratio of hydroxyl groups present in phosphoric acid and epoxy resin is preferably such that epoxy groups remain unreacted. More specifically, it is preferred that an equivalent ratio of hydroxyl groups bonded to phosphorus atoms and epoxy groups be such that the $(\text{hydroxyl group})/(\text{epoxy group}) = 0.05\sim 0.95$. Further, it is especially preferred that the above ratio be such that $(\text{hydroxyl group})/(\text{epoxy group}) = 0.6\sim 0.9$.

[0012] When an alcohol is used as a solvent, there is a possibility of phosphoric acid compounds and phosphoric acid esters being formed. However, even if phosphoric ester compounds are formed, they will dissociate during heating and drying and will react with the excess epoxy groups, causing no degradation of adhesive properties.

[0013] The polyester resins (B) containing hydroxyl groups in accordance with the present invention are straight-chain polyester resins with excess alcohol component, which consist of a dihydric alcohol component such as ethylene glycol, propylene glycol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, neopentyl glycol, Newpol BEP series (ethylene oxide adducts of bisphenol A, manufactured by Sanyo Chemical Co., Ltd.), Newpol BP series (propylene oxide adducts of bisphenol A, manufactured by Sanyo Chemical Co., Ltd.), and the like and a dicarboxylic acid such as isophthalic acid, terephthalic acid, fumaric acid, adipic acid, azelaic acid, sebacic acid, as well as maleic acid, succinic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, and anhydrides thereof. No specific limitation is placed on the number-average molecular weight of the resin, but from the standpoint of mutual solubility with the modified epoxy resin (A) and coating film performance, it is preferred that the number-average molecular weight be within a range of 5,000~30,000. Furthermore, no specific limitation is placed on the content ratio of hydroxyl groups in the polyester resin (B) containing hydroxyl groups, that was thus obtained. However, from the standpoint of adhesion to steel sheets, it is especially preferred that the hydroxyl number (number for solids) be 5~50.

[0014] Alkylolated urea-formaldehyde resins, alkylolated melamine-formaldehyde resins, alkylolated benzoguanamine-formaldehyde resins, and the like can be used as the aminoplast resins which are the curing agent (C) in accordance with the present invention. Furthermore, examples of suitable blocked isocyanate resins include toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, isophorone diisocyanate, and the like, blocked by phenols, lactams, ketoximes, and the like, or combinations thereof. Among those resins, alkylolated melamine-formaldehyde resin is especially preferred because of its excellent processability and adhesive properties.

[0015] No specific limitation is placed on the compounding ratio of the modified epoxy resin (A), polyester resin (B) containing hydroxyl groups, and curing agent (C). However, from the standpoint of adhesive properties and moisture resistance, the content ratio of the modified epoxy resin (A) is preferably 0.1~20 wt.%; from the standpoint of processability and adhesive properties, the content ratio of the polyester resin (B) containing hydroxyl groups is preferably 70~95 wt.%; and from the standpoint of processability and adhesive properties, the content ratio of the curing agent (C) is preferably 5~70 wt.%, all the content ratios being based on the total of (A)~(C).

[0016] No specific limitation is placed on the solvents that can be used, and examples of suitable solvents include ketones, esters, hydrocarbons, ethers, and alcohols. However, ketones and esters are preferred because they demonstrate excellent solubilization ability. Specific examples of ketones include isophorone and cyclohexanone, and specific examples of esters include ethyl acetate and cellosolve acetate.

[0017] Well-known pigments and additives can be used, without any specific limitation, in the composition in accordance with the present invention. Examples of suitable pigments include strontium chromate, titanium dioxide, clay, bentone, and the like. Examples of additives include various pigment dispersing agents, viscosity adjusting agents, and the like.

[0018] The resin composition for coating in accordance with the present invention can be coated on a metal substrate such as hot-dip galvanized steel sheets, electrogalvanized steel sheets, tin-plated steel sheets, chromium steel, stainless steel, aluminum, and the like by the conventional coating methods, for example, roller coating method, spray coating method, and the like.

[0019] Curing of the resin composition for coating in accordance with the present invention can be conducted within a wide range of from 5 sec to 30 min at a temperature of from 150°C to 400°C.

[0020] When the composition in accordance with the present invention is used as an undercoat coating material, after it has been coated on a steel sheet by the above-mentioned method, a topcoat can be formed by using topcoat coating materials such as acrylic resins, silicone polyester resins, polyurethane resins, fluororesins, epoxy resins, polyester resins, and the like. Among them, polyester resins are preferred because of their excellent water resistance, corrosion resistance, and processability. In particular, when a thermosetting resin composition is used which contains a polyester resin (D) containing hydroxyl groups, an aminoplast resin (E), and a

pigment (F) as the necessary components, the effect of the present invention becomes especially significant.

[0021] Thus, the coated steel sheet in accordance with the present invention can be obtained by coating the above-described resin composition for coating on a steel sheet and then coating as a topcoat coating material a thermosetting resin composition comprising a polyester resin (D) containing hydroxyl groups, an aminoplast resin (E), and a pigment (F) as the necessary components.

[0022] No specific limitation is placed on the polyester resin (D) containing hydroxyl groups. The preferred resins, however, are straight-chain polyester resins with excess alcohol component, which consist of a dihydric alcohol component such as ethylene glycol, propylene glycol, 1,6-hexanediol, diethylene glycol, dipropylene glycol, neopentyl glycol, and the like and a dicarboxylic acid such as isophthalic acid, terephthalic acid, fumaric acid, adipic acid, azelaic acid, sebacic acid, as well as maleic acid, succinic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, and anhydrides thereof. No specific limitation is placed on the number-average molecular weight of the resin, but from the standpoint of coating film performance, it is preferred that the number-average molecular weight be within a range of 5,000~30,000.

[0023] Alkylolated urea-formaldehyde resins, alkylolated melamine-formaldehyde resin, alkylolated benzoguanamine-formaldehyde resin, and the like can be used as the aminoplast resin (E). Furthermore, examples of suitable blocked isocyanate resins include toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, isophorone diisocyanate, and the like, blocked by phenols, lactams, ketoximes, and the like, or combinations thereof. Among those resins, alkylolated melamine-formaldehyde resin is especially preferred because of its excellent processability and adhesive properties.

[0024] No specific limitation is placed on pigment (F), and both organic and inorganic pigments may be used. Thus, pigments of various colors, such as titanium oxide, iron oxide red, carbon, cyanine blue, and the like, can be used according to the application. Furthermore, no specific limitation is placed on the additives or compounded substances. Thus, antifoaming agents, lubricating agents, pigment-dispersing agents, and the like can be used according to the application. Examples of suitable antifoaming agents include vinyl acetate emulsions, acrylic emulsions, and the like. Examples of suitable lubricating agents include carnauba wax, microcrystalline wax, acrylamide, and the like. Examples of suitable pigment-dispersing agents include alkylbenzenesulfonates and the like. Those examples are, however, not limiting.

[0025] Similarly to the undercoat compositions, well-known coating methods, such as roller coating method, spray coating method, and the like can be employed for coating the topcoat composition. Cutting of the top coat composition can be conducted within a wide range of from 5 sec to 30 min and from 150°C to 400°C.

[0026] No specific limitation is placed on the thickness of the undercoat layer and topcoat layer. It is, however, typically preferred that the underlayer thickness be 3~20 μm and that of the topcoat layer be 10~30 μm .

[0027]

[Examples] The present invention will be described hereinbelow based on examples thereof. In the examples, the term "parts" stands for weight parts and "%" stands for "wt.%".

[0028] Preparation Example 1 (Preparation of modified epoxy resin solution A-1)

A total of 600 parts of a commercial liquid BPA-type epoxy resin (for example, EPICLON 850, trade name, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 200 parts of bisphenol A, and 4 parts of 2% aqueous solution of sodium hydroxide were placed in a four-neck flask equipped with a stirrer, a thermometer, a nitrogen supply tube, and a reflux cooler, and an epoxy resin with an epoxy equivalent of 600 was obtained by conducting the reaction at a temperature of 150°C, while introducing nitrogen gas. The epoxy resin was dissolved by adding 350 parts of xylene, 200 parts of ethylene glycol monobutyl ether, and 200 parts of 1-butyl alcohol. Upon cooling to a temperature of 80°C, a total of 34 parts of 89% phosphoric acid was added and the reaction was conducted until a stable viscosity was obtained. Then, modified epoxy resin solution A-1 was obtained by adding ethylene glycol monobutyl ether to obtain the content ratio of solids of 50%.

[0029] Preparation Example 2 (Preparation of modified epoxy resin solution A-2)

A total of 600 parts of a commercial liquid BPA-type epoxy resin (for example, EPICLON 850, trade name, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 250 parts of bisphenol A, and 4 parts of 2% aqueous solution of sodium hydroxide were placed in a four-neck flask equipped with a stirrer, a thermometer, a nitrogen supply tube, and a reflux cooler, and an epoxy resin with an epoxy equivalent of 900 was obtained by conducting the reaction at a temperature of 150°C, while introducing nitrogen gas. The epoxy resin was dissolved by adding 350 parts of xylene, 200 parts of ethylene glycol monobutyl ether, and 200 parts of 1-butyl alcohol. Upon cooling to a temperature of 80°C, a total of 24 parts of 89% phosphoric acid was added and the reaction was conducted until a stable viscosity was obtained. Then, modified epoxy resin solution A-2 was obtained by adding ethylene glycol monobutyl ether to obtain the content ratio of solids of 50%.

[0030] Preparation Example 3 (Preparation of modified epoxy resin solution A-3)

A total of 500 parts of a commercial liquid BPA-type epoxy resin (for example, EPICLON 850, trade name, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 250 parts of bisphenol A, and 4 parts of 2% aqueous solution of sodium hydroxide were placed in a four-neck flask equipped with a stirrer, a thermometer, a nitrogen supply tube, and a reflux cooler, and an epoxy resin with an epoxy equivalent of 2000 was obtained by conducting the reaction at a temperature of 160°C, while introducing nitrogen gas. The epoxy resin was dissolved by adding 350 parts of xylene, 200 parts of ethylene glycol monobutyl ether, and 200 parts of 1-butyl alcohol. Upon cooling to a temperature of 80°C, a total of 10 parts of 89% phosphoric acid was added and the reaction was conducted until a stable viscosity was obtained. Then, modified epoxy resin solution A-3 was obtained by adding ethylene glycol monobutyl ether to obtain the content ratio of solids of 50%.

[0031] Preparation Example 4 (Preparation of modified epoxy resin solution B-1)

A total of 600 parts of a commercial liquid BPA-type epoxy resin (for example, EPICLON 850, trade name, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 200 parts of bisphenol A, and 4 parts of 2% aqueous solution of sodium hydroxide were placed in a four-neck flask equipped with a stirrer, a thermometer, a nitrogen supply tube, and a reflux cooler, and an epoxy resin with an epoxy equivalent of 600 was obtained by conducting the reaction at a temperature of 150°C, while introducing nitrogen gas. The epoxy resin was dissolved by adding 350 parts of xylene, 200 parts of ethylene glycol monobutyl ether, and 200 parts of 1-butyl alcohol. Upon cooling to a temperature of 80°C, a total of 73.4 parts of 89% phosphoric acid was added and the reaction was conducted until a stable viscosity was obtained. Then, modified epoxy resin solution B-1 was obtained by adding ethylene glycol monobutyl ether to obtain the content ratio of solids of 50%.

[0032] Example 1

A total of 1 part of modified epoxy resin solution A-1, 44 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd., monomer composition: terephthalic acid, isophthalic acid, ethylene glycol; EO adduct of BPA, hydroxyl value: 8~15), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 150 parts of cyclohexanone, and 150 parts of Solvesso 100 were mixed to prepare an undercoat coating material. The topcoat coating material was prepared by mixing 55 parts of polyester resin containing hydroxyl groups (Beckolite 57-206, manufactured by Dainippon Ink and Chemicals Co., Ltd., monomer composition: terephthalic acid, isophthalic acid, ethylene glycol, neopentyl glycol, hydroxyl value: 30), 5 parts of methylated melamine resin (MS 11, manufactured by Sanwa Chemical Co., Ltd.), 20 parts of titanium dioxide, and 20 parts of isophorone. The undercoat coating material was coated on a hot-dip galvanized steel sheet with a sheet thickness of 0.6 mm and a zinc coating ratio of 90 g/cm², and the coating was dried for 60 sec at a temperature of 200°C to obtain a coating steel sheet with a coating film thickness of 5 μm. The top coating material was then coated and the coating was dried for 120 sec at a temperature of 240°C to obtain a coated steel sheet with a topcoat thickness of 17 μm and a total thickness of the undercoat and topcoat of 23 μm.

[0033] Example 2

An undercoat coating material was prepared by mixing 2 parts of modified epoxy resin solution A-1, 43 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 15 parts of cyclohexanone, and 15 parts of Solvesso 100. A coating material of the same composition as in Example 1 was used for the topcoat coating material. The coating was conducted by the same method as in Example 1.

[0034] Example 3

An undercoat coating material was prepared by mixing 5 parts of modified epoxy resin solution A-1, 40 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 15 parts of cyclohexanone, and 15 parts of Solvesso 100. A coating material of the same composition as in Example 1 was used for the topcoat coating material. The coating was conducted by the same method as in Example 1.

[0035] Example 4

An undercoat coating material was prepared by mixing 2 parts of modified epoxy resin solution A-2, 43 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 15 parts of cyclohexanone, and 15 parts of Solvesso 100. A coating material of the same composition as in Example 1 was used for the topcoat coating material. The coating was conducted by the same method as in Example 1.

[0036] Example 5

An undercoat coating material was prepared by mixing 2 parts of modified epoxy resin solution A-3, 43 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 15 parts of cyclohexanone, and 15 parts of Solvesso 100. A coating material of the same composition as in Example 1 was used for the topcoat coating material. The coating was conducted by the same method as in Example 1.

[0037] Comparative Example 1

An undercoat coating material was prepared by mixing 45 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 15 parts of cyclohexanone, and 15 parts of Solvesso 100. A coating material of the same composition as in Example 1 was used for the topcoat coating material. The coating was conducted by the same method as in Example 1.

[0038] Comparative Example 2

An undercoat coating material was prepared by mixing 2 parts of epoxy resin solution (solids 50%) prior to the reaction with phosphoric acid, which was synthesized in Preparation Example 1, 43 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 15 parts of cyclohexanone, and 15 parts of Solvesso 100. A coating material of the

same composition as in Example 1 was used for the topcoat coating material. The coating was conducted by the same method as in Example 1.

[0039] Comparative Example 3

An undercoat coating material was prepared by mixing 2 parts of modified epoxy resin solution B-1, 43 parts of a solution of polyester resin containing hydroxyl groups (Beckolite M-6801, manufactured by Dainippon Ink and Chemicals Co., Ltd.), 5 parts of methylated melamine resin (Cymel 325, manufactured by Mitsui Toatsu Kagaku Kogyo K. K.), 20 parts of strontium chromate, 15 parts of cyclohexanone, and 15 parts of Solvesso 100. A coating material of the same composition as in Example 1 was used for the topcoat coating material. The coating was conducted by the same method as in Example 1.

[0040] Physical properties of coating films on the coated steel sheets obtained in Examples 1~5 and Comparative Examples 1~3 were tested. The results are shown in Table 1 and Table 2. The tests of physical properties of the coating films were conducted by the following methods.

[0041] · Stability of coating material: all coating materials were stored for 1 month at a temperature of 40°C and then observations of separation and gelling state in the coating materials were conducted. The evaluation criteria were as follows.

⊙: no abnormalities

○: slight setting

Δ: setting (soft cake)

×: setting (hard cake)

[0042] · Processability: an OT bending test was conducted at 25°C and the presence of cracks in the processing zone was observed. The evaluation criteria were as follows.

⊙: no abnormalities

○: slight cracking was observed with a 20x magnifying glass

Δ: cracks appeared

×: coating film peeled

[0043] · Moisture resistance: flat portion was examined after 240 h at 45°C, 98%RH have elapsed. The evaluation criteria were as follows.

⊙: no abnormalities; evaluation 10 according to ASTM D-714

○: gloss decrease; evaluation 10 according to ASTM D-714

Δ: no abnormalities in visual inspection, slight cracking was observed with a 20x magnifying glass; evaluation 10 according to ASTM D-714

×: bulging is observed in visual inspection; evaluation 8F according to ASTM D-714

[0044] Corrosion resistance: a salt water spraying test was conducted at a temperature of 40°C and the cut section surface was observed after 240 h. The evaluation criteria were as follows.

[0045] ⊙ : no abnormalities

○ : white rust appeared, no bulging

△ : red rust appeared, no bulging

× : bulging

[0046]

[Table 1]

Table 1. Testing of physical properties of coating film on coated steel sheet

	Embodiment 1	Embodiment 2	Embodiment 3	Embodiment 4	Embodiment 5
Stability of coating film	⊙	⊙	⊙	⊙	○
Processability	⊙	⊙	⊙	⊙	⊙
Moisture resistance	○	⊙	⊙	⊙	⊙
Corrosion resistance	⊙	⊙	⊙	⊙	⊙

[0047]

[Table 2]

Table 2. Testing of physical properties of coating film on coated steel sheet

	Comparative Example 1	Comparative Example 2	Comparative Example 3
Stability of coating film	⊙	⊙	×
Processability	⊙	⊙	⊙
Moisture resistance	×	×	×
Corrosion resistance	○	○	○

[0048] Effect of the Invention] The object of the present invention is to provide a coated steel sheet which demonstrates excellent adhesion of the coating to the steel sheet and stability of the coating material and also excellent water resistance and processability as a precoated metal.